

# Distribution function theory of liquids

Partition function

$$Q = \sum_j e^{-\beta E_j}$$

"Quantization"  
"Energy" QM

Purely classical system

$$\begin{aligned} r^N &\equiv 3N \text{ position} \\ &\quad \text{co-ordinates} \\ p^N &\equiv 3N \text{ momenta} \\ &\quad \text{co-ordinates} \end{aligned}$$

Hamiltonian  
of the system

$$H[r^N, p^N] = K[p^N] + U[r^N]$$

K.E. P.E.

Canonical partition function for a purely classical system

$$Q = Q_{\text{Classical}} = \frac{1}{N! h^{3N}} \int d\tau^N \int dp^N \exp[-\beta H(r^N, p^N)]$$

if we assume the particles are indistinguishable

$$\delta r^N \delta p^N \sim h^{3N}$$

$f(\gamma^N, p^N)$  = probability distribution for observing a system at phase space point  $(\gamma^N, p^N)$ .

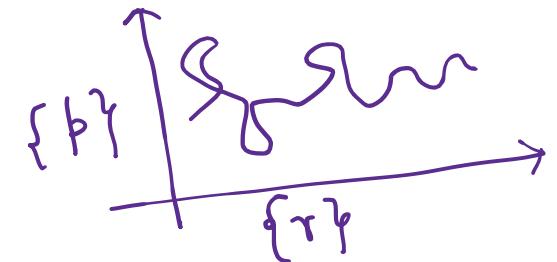
$$f(\gamma^N, p^N) = \frac{\exp[-\beta H(\gamma^N, p^N)]}{\int d\gamma^N \int dp^N \exp[-\beta H(\gamma^N, p^N)]}$$

$$= \frac{\exp[-\beta(K(p^N) + U(\gamma^N))]}{\int d\gamma^N \int dp^N \exp[-\beta(K(p^N) + U(\gamma^N))]}$$

$$= \frac{\exp[-\beta K(p^N)]}{\int dp^N \exp[-\beta K(p^N)]} \times \frac{\exp[-\beta U(\gamma^N)]}{\int d\gamma^N \exp[-\beta U(\gamma^N)]}$$

$\phi(p^N) \quad P(\gamma^N)$

$$f(\gamma^N, p^N) = \phi(p^N) P(\gamma^N)$$



$$\int d\gamma^N \equiv \int dr_1 \int dr_2 \cdots \int dr_N$$

$$\int dp^N \equiv \int dp_1 \int dp_2 \cdots \int dp_N$$

$$\int dr \equiv \int dx \int dy \int dz$$

$$\int dp \equiv \int dp_x \int dp_y \int dp_z$$

$\phi(p^N)$  = prob. distribution for observing system at momentum space point  $p^N$

$P(r^N)$  = prob. distribution for observing system at configuration space point  $r^N$ .

Reduced configurational distribution functions:

$$P^{(2|N)}(r_1, r_2) = \int dr_3 \int dr_4 \dots \int dr_N P(r^N)$$

↓  
joint probability  
distribution for

finding particle 1  
at  $r_1$  and particle  
2 at  $r_2$

Specific probability  
distribution (specifically requires particle 1  
at  $r_1$  and particle 2 at  $r_2$ ).

generic reduced distribution functions:

$P^{(2/N)}(\tau_1, \tau_2) \equiv$  joint prob. distribution function  
for finding a particle (anyone)  
at position  $\tau_1$  and any other  
particle at position  $\tau_2$  (in the  
 $N$  particle system)

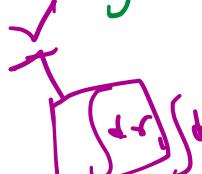
$$P^{(2/N)}(\tau_1, \tau_2) = N(N-1) P^{(2/N)}(\tau_1, \tau_2) \xrightarrow{\frac{N!}{(N-2)!}}$$

$$P^{(n/N)}(\tau_1, \tau_2, \dots, \tau_n) = \frac{N!}{(N-n)!} \frac{(N-1)!}{\int d\tau^{N-n} \exp[-\beta U(r^N)]}$$

$$\boxed{\int d\tau^N \exp[-\beta U(r^N)]}$$

$$Z_N \equiv V^N \quad (\text{for ideal gas})$$

$$\int d\tau^{N-n} = \int d\tau_{n+1} \int d\tau_{n+2} \dots \int d\tau_N$$


 $\int d\tau_2 \cdot \dots \cdot e^0$   
 $Z_N \uparrow$  (configurational integral)

$$P^{(n/N)}(\tau_1, \tau_2, \dots, \tau_n) = \frac{N!}{(N-n)!} \frac{1}{Z_N} \int d\tau_{n+1} \int d\tau_{n+2} \dots \int d\tau_N \exp(-\beta U(\tau^N))$$

$(\tau_1, \tau_2, \dots, \tau_N)$

↓  
"Integrate"

$$\int \dots \int P^{(n/N)}(\tau_1, \tau_2, \dots, \tau_n) d\tau_1 \dots d\tau_n = \frac{N!}{(N-n)!} \frac{1}{Z_N} \int d\tau_1 \dots \int d\tau_{n+1} \dots \int d\tau_N \exp(-\beta U(\tau_1, \tau_2, \dots, \tau_N))$$

$Z_N$

$\int P^{(n/N)}(\tau^n) d\tau^n = \frac{N!}{(N-n)!}$

$$\int P^{(1/N)}(\tau_i) d\tau_i = N \quad (\text{number conservation})$$

$$P^{(N)}(r_1) = \frac{N!}{(N-1)!} \frac{1}{Z_N} \int d\tau_2 \int d\tau_3 \dots \int d\tau_N \exp(-\beta U(r_1, r_2, \dots, r_N))$$

For homogeneous liquid

$$Z_N = \left\{ \int d\sigma_1 \right\} \int d\tau_2 \dots \dots \dots \int d\tau_N e^{-\beta U(r_1, r_2, \dots, r_N)}$$

$$Z_N = V \int d\tau_2 \int d\tau_3 \dots \int d\tau_N e^{-\beta U(r^N)}$$

$$\rho^{(N)}(r) = \frac{N}{Z_N} \frac{Z_N}{V} = \frac{N}{V} = \rho \text{ (density)}$$

$$P^{(2/N)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{N!}{(N-2)!} \frac{1}{Z_N} \int d\mathbf{r}_3 \int d\mathbf{r}_4 \dots \int d\mathbf{r}_{N-2} e^{-\beta U(r^N)}$$

$$= \frac{N(N-1)}{Z_N} \int d\mathbf{r}_3 \int d\mathbf{r}_4 \dots \int d\mathbf{r}_{N-2} e^{-\beta U(r^N)}$$

In case of ideal gas (fluid with interparticle interaction)

$$P^{(2/N)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{\cancel{Z_N}} \frac{V^{N-2}}{V^N} = N(N-1) \frac{V^{N-2}}{V^N} = \frac{N(N-1)}{V^2} \simeq \frac{N^2}{V^2} = \rho^2$$

"N is very large"

$$= \rho^{(1/N)}(\mathbf{r}_1) \rho^{(1/N)}(\mathbf{r}_2) \quad (U=0)$$

Let us define,

$$g(r_1, r_2) = \frac{\rho^{(2/N)}(r_1, r_2)}{\rho^2}$$

$$g(r_1, r_2) = \rho^r / \rho^2 = 1$$

(ideal gas)

Also,  $h(r_1, r_2) = \frac{(\rho^{(2/N)}(r_1, r_2) - \rho^r)}{\rho^2} = g(r_1, r_2) - 1$

$\rho$  = Bulk density

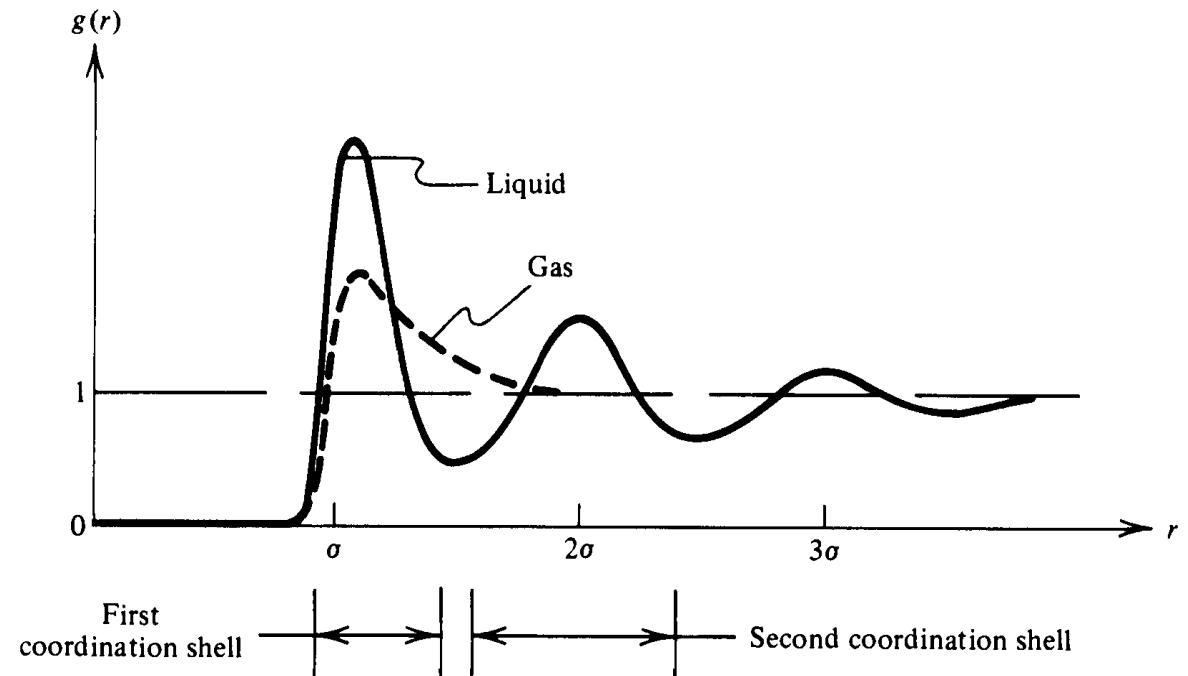
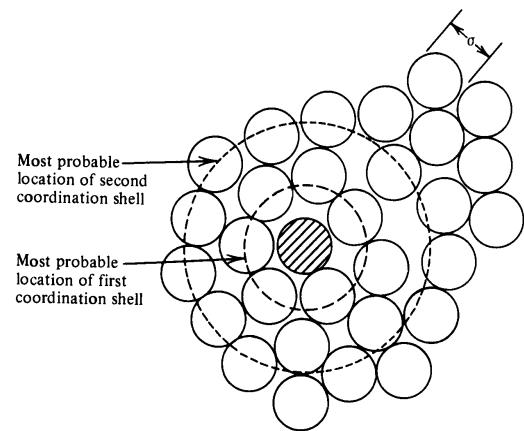
$g(r_1, r_2)$   $\hookrightarrow$  Pair-correlation fn/radial distribution function

$$\rho^{(2/N)}(0, r) = \rho^r g(r)$$

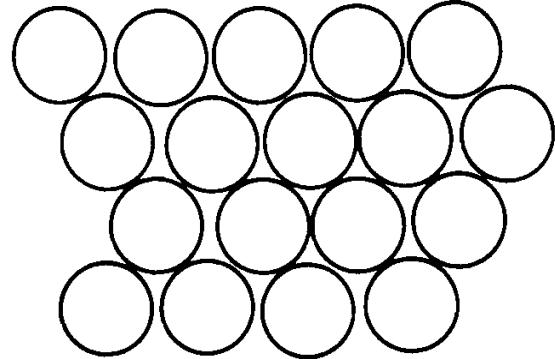
$\frac{\rho^{(2/N)}(0, r)}{\rho} = \rho g(r) = \text{conditional prob. that a particle will be found at } r \text{ given that another is at the origin}$

Liquid Structure  $\equiv g(r)$

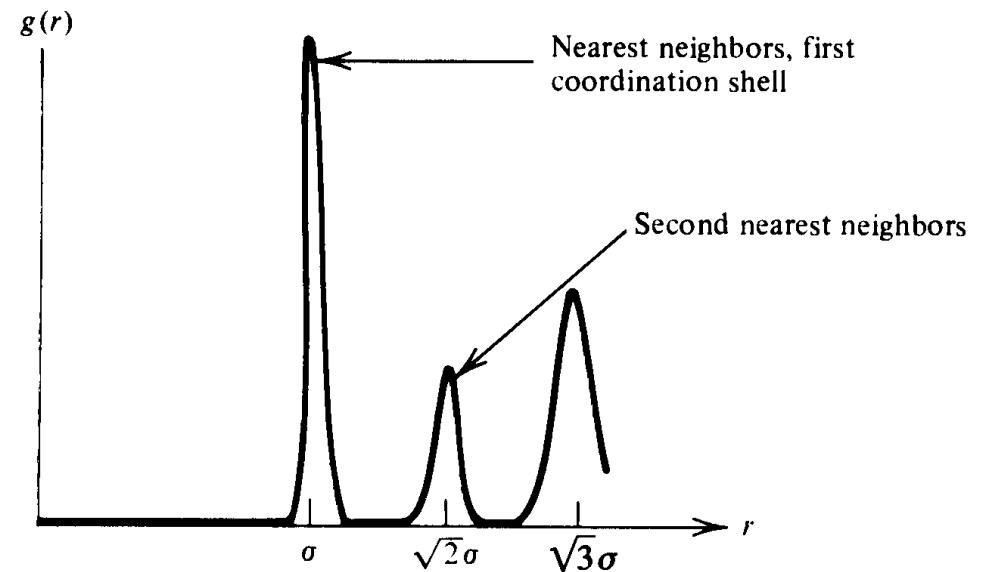
$\equiv$  average density of particles at  $r$  given that a tagged particle is at the origin



David Chandler → Introduction to SM



Crystalline order: solid



Highly ordered solid